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(54) POLYAMINE CURING AGENTS FOR ISOCYANATO-TERMINATED PREPOLYMERS

(71) We, E. I. DU PONT DE NEMOURS & Co., a Corporation organized and existing under the laws of the States of Delaware, United States of America, of Wilmington 98, Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Our prior application Number 24223/67, filed May 1967, Serial No. 1,142,667 describes a process for producing a mixture of diamines which are excellent curing agents, of moderate reactivity, for liquid isocyanato-terminated prepolymers. The resultant polyurethane forming compositions may be cast, or may be foamed and then sprayed to coat a substrate. This prior process is carried out by reacting two monoamines, namely aniline and 2-chloroaniline (o-chloroaniline) with formaldehyde in the presence of a mineral acid, the mole ratio of aniline to 2-chloroaniline being 0.1 to 4.0:1, and the mole ratio of total amines to formaldehyde being 1.4 to 1.9:1, or 1.6 to 1.9:1 for making curing agents for castable polyurethanes, most preferably 1.65 to 1.9:1. Thus according to this prior specification, the 2-chloro-aniline may constitute 20 to about 90 mole % of the amine mixture, and the aniline may constitute 80 to about 10 mole %.

We have now found that it is possible to omit the aniline from the monoamine reactant or to introduce o-toluidine (2-methyl aniline) into the amine reactant. This last mentioned compound may be used to a large extent (up to 80 mole % of the amine) to replace the 2-chloroaniline or aniline.

We have also found that, provided the total amine for formaldehyde ratio does not exceed 1.8, it is possible to use more than 90 mole percent of the 2-chloroaniline in the mixture (i.e. to use less than 10 mole % of the aniline and/or o-toluidine).

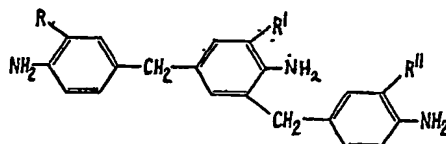
According to this invention there is provided a process for the production of an amine curing agent, which comprises condensing a monoamine reactant with formaldehyde in the presence of a mineral acid, the monoamine reactant consisting of:

- 20—100 mole % 2-chloroaniline, preferably 50—90 mole %,
- 0—80 mole % aniline, preferably 0—50 mole %, and
- 2—80 mole % o-toluidine, preferably 0—50 mole %

the molar ratio of monoamine reactant to formaldehyde being 1.3 to 2.0:1, but not exceeding 1.9:1 when the monoamine reactant is a mixture of 2-chloroaniline and aniline only, and not exceeding 1.8:1 when the monoamine reactant consists of more than 90% of 2-chloroaniline, and the mole ratio of mineral acid to monoamine reactant being 0.5—2.0:1.

Expressed in another way, there may be used from 0.0 to about 4.0 moles of aniline and/or o-toluidine for each mole of 2-chloroaniline present. The compositions of the present invention are believed to be mixtures containing one or more diamines, related triamines and higher polyamines in varying proportions. The diamines which may be present as in the aforesaid Application, are, 4,4'-methylenedianiline, 4,4'-methylenebis(2-chloroaniline) and 3-chloro-4,4'-diaminodiphenylmethane; furthermore according to this invention 4,4'-methylenbis(2-methylaniline), 3-chloro-3'-methyl-

4,4'-diaminodiphenylmethane and 3-methyl-4,4'-diaminodiphenylmethane may be present. The triamines are believed to have the following structure in which R, R' and R'' are H, Cl or methyl:



The higher polyamines are believed to have structures similar to that proposed for the triamines.

- 10 The compositions can be made by the procedures set forth in the aforesaid Application except that 2-toluidine may be included with the monoamine reactant or aniline omitted from the monoamine reactant. The amount of mineral acid used is as described in the aforesaid Application.

15 It is important to control the mole ratio of each of the monoamines, namely aniline, 2-chloroaniline and *o*-toluidine, to obtain curing agents having the required properties.

20 As the amount of 2-chloroaniline used in the amine composition increases, the product becomes higher melting and crystallizes more rapidly. When a lesser amount of aniline and/or *o*-toluidine than 10 mole percent is used and the ratio of total moles of monoamine to formaldehyde is in the range of about 1.8 to 1.9 or 2.0, the product contains large amounts of 4,4'-methylenebis(2-chloroaniline) with the result that it is higher melting, crystallizes more rapidly and differs only slightly in reactivity from pure 4,4'-methylenebis(2-chloroaniline). To compensate for this effect, the ratio of total moles of amine to formaldehyde is adjusted downward to not exceed 1.8 when less than 10 mole percent of the amine composition is aniline and/or *o*-toluidine. As the mole ratio of aniline and/or 2-toluidine to 2-chloroaniline is increased within the limits specified, the reactivity of the mixtures of amines, and the concentration of tri- and polyamines and with it the viscosity, is increased. This results in an increase in viscosity of the condensation products. The higher the molar ratios of aniline and/or 2-toluidine to 2-chloroaniline, the lower are the tendency to crystallize and the rate of crystallization. If less than 20 mole percent 2-chloroaniline is used in the amine composition, products differing only slightly in reactivity from pure 4,4'-methylenediamine, 3-methyl-4,4'-diaminodiphenylmethane or 4,4'-methylenebis(2-methylaniline) are obtained, depending on the relative proportions of aniline and *o*-toluidine present.

55 It is frequently of commercial advantage, when aniline is employed as a reactant, to use crude 2-chloroaniline which is the product obtained directly by the standard iron or hydro-

gen reduction of 2-chloronitrobenzene without fractional distillation of the product. A representative process of this type is given in U.S. Patent 3,073,865. The crude 2-chloroanilines of this type can contain as much as 15% or more of aniline and about 2% or less of non-volatile tarry materials which are formed during the reduction process. The amount of aniline in the crude 2-chloroaniline is taken into account in proportionally reducing the quantity of aniline (if any) to be added from another source.

Condensation products prepared from about equimolar mixtures of 2-chloroaniline and 2-toluidine at mole ratios of total amine to formaldehyde approaching 2:1 contain significant quantities of 3-chloro-3'-methyl-4,4'-diaminodiphenylmethane. A diamine fraction rich in 3-chloro-4,4'-diaminodiphenylmethane is readily obtained as a crystalline material having a melting point of 77—79°C. by vacuum distillation of the proper condensation product; substantially pure 3-chloro-4,4'-diamino-diphenylmethane can then be obtained by fractional extraction with a weak acid. The melting point can be raised to 82—83°C. by recrystallization. A diamine fraction enriched in 3-chloro-3'-methyl-4,4'-diaminodiphenylmethane having a melting range of about 84—100°C. can be obtained by vacuum distillation. Both compounds are useful curing agents for urethane prepolymers but they crystallize rapidly in contrast to the other curing agents of this invention.

If the mole ratio of total amine to formaldehyde falls below 1.3, the condensation products contain very high concentrations of polyamines and are too viscous to be manufactured conveniently or for practical use. Indeed for some purposes, e.g. the preparation of castable polyurethanes, the ratio should be greater than 1.6. If the ratio is above 2.0, diamines predominate in the condensation product, and there are not sufficient tri- and polyamines present to prevent rapid crystallization.

It is preferred to use molar ratios of aniline and/or *o*-toluidine to 2-chloroaniline of 0.1 to 1.0: It is also preferred to use molar ratios of total amines to formaldehyde of 1.65 to 1.9, since below ratios of 1.9 the compositions have higher viscosities and greater resistance to crystallization; the viscosities of the preferred compositions match or approach those of any prepolymers, which facilitates mixing of the curing agent and prepolymer. The composition of the reaction mixtures using the preferred ranges of reactants, after completion of the condensation and rearrangement, consists essentially of the desired di- and polyamine mixtures, with such small amounts of unreacted monoamines that steam or vacuum distillation is not usually necessary. When the molar ratio of monoamine to formaldehyde is more than 1.65, it is sometimes desirable to use all three of the monoamines since the products

usually have lower melting points than if only two or one of the monoamines are used.

The process described in U.S. Patent No. 2,850,464 illustrates the use of polyamines in general in the preparation of polyurethane foam in water-blown prepolymer systems. In an analogous manner, polyamines can be in the preparation of foams by semi-prepolymer and one-shot procedures by replacing part of the active hydrogen normally provided by the polyol with a polyamine. While the amine mixtures of this invention can be used to advantage for preparing flexible or rigid foams, they have been found to be particularly useful in the preparation of self-skinned, semi-rigid molded foam articles. The over-all density of these molded foams can be controlled by adjusting the quantity of expanding agent and is known for conventional polyurethane foams. The skin thickness can be increased by lowering mold temperature and/or increasing the heat capacity and thermal conductivity of the mold. Semi-rigid foam formulations including the amine mixtures of this invention build viscosity and develop gel strength quickly leading to efficient utilization of volatile expanding agents and permitting rapid demolding. However, gelling does not take place prematurely so as to prevent full expansion as is the case with prior art diamines such as 4,4'-methylenedianiline and 4,4'-methylenebis(2-chloroaniline). The self-skinned molded articles prepared using the present amine mixtures accurately reproduce mold surfaces. The skin portions of such molded articles do not evidence any tendency to separate from the lower density interior portions. As previously noted, the compression set of foams cured with the amine mixtures of this invention is lower than that of foams cured with prior art diamines.

The curing agents are employed in substantially the same manner as are conventional diamine curing agents. They are particularly useful in preparing polyurethane foams and cast elastomers by curing isocyanato-terminated prepolymers based on either polyether or polyester glycols. The curing agents may be used to prepare vulcanisates and polyurethane foams in the manner described in the aforesaid U.K. Patent Specification No. 1,142,667. However, in making foams the lower limit of the ratio of total amine to formaldehyde can be 1.3, not 1.4 as in the aforesaid Patent, and when 2-chloroaniline is the only amine used, this ratio should not exceed 1.8. In some instances, particularly when the amine curing agent is very viscous, it may be advantageous to add the polyol to the curing agent reaction mixture after neutralization of the acid. This procedure frequently facilitates separation of the viscous amine curing agents from the neutralized reaction mass.

Thus the invention includes (a) a process for the preparation of castable polyurethane compositions which comprises mixing a liquid

isocyanato-terminated prepolymer with an amine curing agent (in the production of which the ratio of the total amine to formaldehyde is 1.6 to 2.0) in such proportions that the mixture contains 0.8 to 1.2 equivalent of amine groups per equivalent of isocyanato groups; and (b) a process for the preparation of a polyurethane foam which comprises reacting a polyisocyanate, a polyol and an amine curing agent in the presence of an expanding agent. Furthermore it includes the production of coated articles by applying to a substrate a composition which is obtained by process (a) above.

In the following Examples parts and percentages are by weight unless otherwise specified.

The following isocyanato-terminated prepolymer is used in the Examples.

Prepolymer A is made by reacting 1 mole of polytetramethylene-ether glycol having a number average molecular weight of about 1000 with 1.6 moles of 2,4-tolylene diisocyanate. It has a free —NCO content of about 4.1% and a Brookfield viscosity of about 6200 cps. at 50°C.

The vulcanizates are obtained by the following procedure. The amine curing agent and prepolymer are weighed prior to mixing and their temperatures are adjusted to the temperatures shown in the examples. The prepolymer is placed in a vessel and the liquid curing agent is added as rapidly as possible with agitation. Agitation is continued until the mix is uniform, when the mix is poured into preheated moulds designed for forming test specimens. Curing of the cast material is accelerated by heating, in an oven when open moulds are used or in a press when closed moulds are used. Curing times and temperatures are specified in the examples. The pot life which is reported in the examples represents the elapsed time from the start of mixing until the mixture becomes too viscous to be poured into moulds.

Examples 1 to 3 show the use of 2-chloroaniline as the sole amine, and Examples 4 to 6 the use of mixtures of 2-chloroaniline and 2-toluidine. Example 7 shows the use of the compositions of Example 3 for curing a foam.

EXAMPLE 1

To a mixture of 2-chloroaniline (510 parts), 97% sulphuric acid (450 parts) and water (850 parts), 37% aqueous formaldehyde (191 parts) is added with agitation at 35–40°C. These amounts correspond to a molar ratio of *o*-chloroaniline to formaldehyde of 1.7:1.0. The temperature is raised to 85°C. within 30 minutes and maintained at 85–95°C. for 4 hours. The reaction mixture is then poured into a solution of 360 parts of sodium hydroxide in 500 parts of water. The organic layer is separated from the aqueous layer and washed with an equal volume of hot water. The organic layer is freed of water by distilla-

tion at 150°C./0.5 mm. Hg and then filtered. No unreacted 2-chloroaniline is recovered during the distillation.

- 5 The product has an average molecular weight of 316. The assay for nitrogen is 10.15% and the calculated functionality is 2.32. When the molten product is cooled to 60°C. and agitated at 60°C., the first crystals appear after 85 minutes. This is in contrast to

4,4'-methylene-bis(2-chloroaniline) which deposits crystals before the temperature of the molten material reaches 60°C. 10

A vulcanizate prepared by mixing 6.34 parts of the curing agent of this Example with 50 parts of the aforementioned prepolymer A at 60°C. followed by curing for 3 hours at 100°C. has the following properties: 15

ASTM

D—412	Tensile Strength, Kg/cm ²	401
D—412	Modulus, 300%, kg/cm ²	155
D—412	Set at Break, %	3
D—470	Tear Strength, D—470 kg/m	625
D—676	Hardness, Durometer A	87
D—395	Compression Set B, 70°C/22 hr. %	25
D—1054	Bashore Resilience, %	40

- 20 A cross-head speed of 50.3 cm/min is used for the stress-strain measurements obtained by ASTM D—412.

EXAMPLE 2

- 25 The procedure of Example 1 is repeated except that the amount of 37% aqueous formaldehyde is increased to 205 parts. This gives a molar ratio of 2-chloroaniline to formaldehyde of 1.5:1. The product has a Brookfield viscosity of 4350 cps. at 50°C. and an average molecular weight of 333. The assay for nitrogen is 10.4% and the calculated functionality is 2.45. When the molten product is cooled to 60°C. and agitated at 60°C., several hours elapse before the first crystals appear. The curing agent of this Example is particularly 30 useful in the preparation of urethane foam by procedures such as those described in Examples 11 and 12 of UK Patent Specification 1142667.

EXAMPLE 3

- 40 To a mixture of 2-chloroaniline (510 parts), 97% sulphuric acid (445 parts) and water (650 parts), 36.6% aqueous formaldehyde (242 parts) is added with agitation at 40—50°C. These amounts correspond to a molar ratio of 45 *o*-chloroaniline to formaldehyde of 1.35:1.0. Within an hour, the temperature is raised to 85°C. and maintained at 85—90°C for 2 more hours. The reaction mixture is then poured into a solution of 360 parts of sodium hydroxide in 500 parts of water. The organic layer is separated, washed with an equal volume of hot water and dried by distillation

at 120°C. and 1 mm. Hg. and then filtered. No *o*-chloroaniline is obtained during the distillation. 55

The product has a Brookfield viscosity of 1270 cps. at 75°C. and an average molecular weight of 367. The assay for nitrogen is 10.2% and the calculated functionality is 2.67. The product does not show any sign of crystallization after standing at room temperature for several months. 60

EXAMPLE 4

To a mixture of 2-chloroaniline (190.5 parts), *o*-toluidine (53.5 parts), 37% hydrochloric acid (197 parts) and water (400 parts), 37% aqueous formaldehyde (80 parts) is added with agitation at 10°C; the molar ratio of *o*-toluidine to 2-chloroaniline is 1:3 and the molar ratio of total monoamine to formaldehyde is 2:1. After the formaldehyde addition, the temperature is raised to 80°C. within 30 minutes and maintained at 80°C. for 5 hours. About 85 parts of sodium hydroxide pellets are added to the reaction mass and the organic layer is separated from the aqueous layer. The organic layer is washed with hot water and dried by distillation at 120°C./2 mm. Hg. 65

The product has a melting range of 72—85°C.; it exhibits a lesser tendency to crystallize than do such hindered prior art curing agent as 4,4'-methylenebis(2-chloroaniline). When 9.2 parts of this material are mixed at 100°C. with 75 parts of prepolymer A and cured for 3 hours at 100°C., a vulcanizate is obtained which has: 70 75 80 85

ASTM

D-412	Tensile strength kg/cm ²	197
D-412	Modulus, 300% kg/cm ²	108.5
D-470	Tear strength kg/m	1160
D-676	Hardness, Durometer A	84

EXAMPLE 5

To a mixture of 2-chloroaniline (127 parts), 37% hydrochloric acid (100 parts) and water (300 parts), 37% aqueous formaldehyde (80 parts) is added with agitation at 25–30°C. The reaction mass is agitated for 15 minutes at 25–30°C. and then *o*-toluidine (107 parts) and additional 37% hydrochloric acid are added. The molar ratio of total amine to formaldehyde is 2:1. The reaction mass is heated to 80°C. within 30 minutes and maintained at 80°C. for 5 hours. The charge is neutralized by adding 83 parts of sodium hydroxide. The organic layer is separated and washed twice with hot water.

About 201 parts of the resulting product are distilled at 0.4 mm. Hg. The first fraction amounts to 155 parts of diamines having a boiling point of 189°C. This fraction has a melting point of 84–100°C. and contains about 50% 3-methyl-3'-chloro-4,4'-methylenedianiline, 30% 4,4'-methylenebis(2-chloroaniline) and 20% 4,4'-methylenebis(2-methylaniline) as determined by gas chromatography.

correspond to a mole ratio of *o*-toluidine to 2-chloroaniline of 1:3 and a molar ratio of total monoamine to formaldehyde of 1.65:1. The temperature is then raised to 85°C. within 1 hour and the reaction mass is maintained at 85–90°C. for two hours. The reaction mass is neutralized by the addition of a solution of 360 parts of sodium hydroxide in 400 parts of water. The organic layer is separated and washed twice with 1000 parts of water at 90°C. The organic layer is dried by heating to 120°C. at a pressure of 1 mm. Hg and filtered. No monoamine is recovered.

The product has a Brookfield viscosity of 5700 cps. at 50°C. and an average molecular weight of 325. The assay for amino group nitrogen is 10.6% and the calculated functionality is 2.46.

The product does not show any signs of crystallizing after standing at room temperature for 12 weeks. It is especially useful in the preparation of urethane foam by the procedures described in Examples 11 and 12 of UK Patent Specification 1142667.

EXAMPLE 6

To a mixture of 2-chloroaniline (382.5 parts), *o*-toluidine (107 parts), 97% sulphuric acid (445 parts) and water (650 parts), 36.6% aqueous formaldehyde (198 parts) is added with agitation at 40–50°C. These amounts

EXAMPLE 7

A semi-rigid foam is prepared from the product of Example 3 by a batch one-shot procedure employing the following formula-

MIXTURE 1

Polypropylene ether triol, number average molecular weight 4500, hydroxyl No. 38, prepared by reacting propylene oxide with glycerine and capping with ethylene oxide to give primary hydroxyl groups (commercially available as "Voranol" CP-4601)	100 parts
("Voranol" is a Registered Trade Mark)	
Polydimethylsiloxane, 50 centistoke grade	1 part
Triethylene diamine, 33% in dipropylene glycol	1.5 parts
Dibutyl tin dilaurate	0.1 part
Amine mixture of Example 3	21.6 parts

MIXTURE 2

Tolylene diisocyanate isomer mixture
(80% 2,4—; 20% 2,6—)

20.4 parts

Fluorotrichloromethane

10 parts

Mixture 1 is heated to 43—44°C. and Mixture 2 (at room temperature) is then added to Mixture 1 and the entire mass is vigorously agitated for about 6 seconds and then poured in a mould and allowed to foam. The density and stress-strain properties of the resulting foam are similar to those of the foams prepared in Examples 11 and 12 of U.K. Patent Specification 1,142,667. The rates of foam rise and curing to a tack-free state are somewhat slower than those observed with the amine mixture used in Examples 11 and 12. The finished foam is covered with a smooth, adherent skin similar to that observed for the foams prepared in Examples 11 and 12.

As already indicated, U.K. Patent Specification 1,142,667 claims a process for the production of an amine curing agent, which comprises condensing aniline and 2-chloroaniline with formaldehyde in the presence of a mineral acid, the mole ratio of aniline to 2-chloroaniline being 0.1 to 4.0, the mole of total amine to formaldehyde being 1.4 to 1.9, and the mole ratio of mineral acid to total amine being 0.5 to 2.0, and also amine curing agents so obtained. It also claims the preparation of castable polyurethane compositions by mixing a liquid isocyanato-terminated prepolymer with such an amine curing agent (in the production of which the ratio of total amine to formaldehyde is 1.6 to 1.9) in such proportions that the mixture contains 0.8 to 1.2 equivalents of amine groups per equivalent of isocyanato groups; a process for the preparation of a polyurethane foam by reacting a polyisocyanate, a polyol and such an amine curing agent in the presence of an expanding agent; castable polyurethane compositions, and polyurethane foams, obtained by the respective processes described above, and the production of coated articles by applying to a substrate by spraying a castable polyurethane forming composition as indicated above.

This subject matter is not claimed here.
Subject to the foregoing disclaimer

WHAT WE CLAIM IS:—

1. Process for the production of an amine curing agent, which comprises condensing a monoamine reactant with formaldehyde in the presence of a mineral acid, the monoamine reactant consisting of:

20—100 mole % 2-chloroaniline,
0—80 mole % aniline, and
0—80 mole % o-toluidine,

the molar ratio of monoamine reactant to formaldehyde being 1.3 to 2.0:1 but not exceeding 1.8:1 when the monoamine reactant consists of more than 90% of 2-chloroaniline and not exceeding 1.9:1 when the monoamine reactant is a mixture of 2-chloroaniline and aniline only, the mole ratio of mineral acid to monoamine reactant being 0.5 to 2.0:1.

2. Process according to claim 1, wherein the monoamine reactant consists of:
50—90 mole % 2-chloroaniline
0—50 mole % aniline, and
0—50 mole % o-toluidine.

3. Process according to claim 1 or 2, wherein the molar ratio of monoamine reactant to formaldehyde is 1.65 to 1.9:1.

4. Process according to claim 1, 2 or 3 wherein the mole ratio of aniline and/or o-toluidine to 2-chloroaniline is 0.1 to 1.0:1.

5. Process according to any one of the preceding claims, wherein at least a portion of the monoamine reactant is crude 2-chloroaniline prepared by reduction of 2-chloronitrobenzene by iron or hydrogen, without fractional distillation of the product.

6. Process for the production of an amine curing agent according to claim 1, substantially as hereinbefore described.

7. An amine curing agent obtained by a process claimed in any one of claims 1 to 6.

8. A process for the preparation of castable polyurethane-forming compositions which comprises mixing a liquid isocyanato-terminated prepolymer with an amine curing agent claimed in claim 7 (in the production of which the ratio of the total amine to formaldehyde is 1.6—2.0) in such proportions that the mixture contains 0.8 to 1.2 equivalent of amino groups per equivalent of isocyanato groups.

9. A process for the preparation of a polyurethane foam which comprises reacting a polyisocyanate, a polyol and an amine curing agent claimed in claim 7 in the presence of an expanding agent.

10. Castable polyurethane-forming compositions obtained by a process claimed in claim 8.

11. Polyurethane foam obtained by a process claimed in claim 9.

12. Process for the production of coated articles, which comprises applying to a substrate by spraying a composition claimed in claim 10.

13. Coated articles obtained by a process claimed in claim 12.

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